Threshold character of the visible fluorescence[1)] excited by IR laser radiation

N.G. Basov, V.T. Galochkin, S.I. Zavorotnyi, V.N. Kosinov, A.A. Ovhinnikov, A.N. Oraevskii, A.V. Pankratov, A.N. Skachkov, and G.V. Shmerling

P. N. Lebedev Physics Institute, USSR Academy of Sciences
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An earlier study[1] of the photochemical action of infrared laser radiation has revealed the existence of a threshold for the laser-chemical process. Further investigations[2] have confirmed the threshold character of the reactions initiated by IR laser radiation.

This raises the following question: are these threshold phenomena singularities of the secondary stages of the laser-chemical process or does the molecule activation via resonant action of the IR laser have by itself a threshold character?

To answer this question it is necessary to investigate the singularities of the excitation of high vibration levels in molecules under resonant action of laser radiation on the vibrational degrees of freedom. It was found convenient to use for this purpose the visible and ultraviolet fluorescence produced when resonant IR radiation acts on a molecule.[3–9]

Convenient objects for the study of the fluorescence are boron trichloride BCl_3 and sulphur hexafluoride SF_6, which absorb resonantly CO_2 laser radiation. To perform experiments in a wide range of radiation, we used IR pulses ($\lambda = 10.6$ μ) of 5 μsec duration and energy 2–3 J, as well as 0.01–1 sec pulses with energy up to 2 J in the pulse. Microsecond pulses were obtained with the aid of a CO_2 laser with transverse discharge; pulses in the range 0.01–1 sec were shaped by modulating a cw CO_2 laser with a disk modulator.

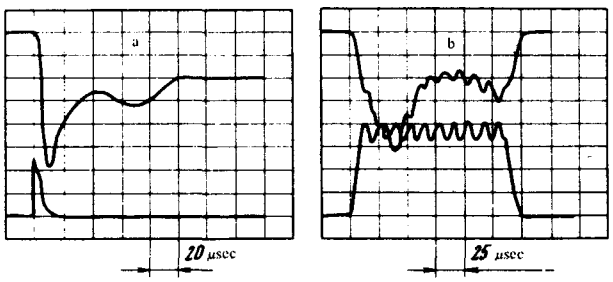

FIG. 1. Typical oscillograms of visible fluorescence pulses: I—CO_2 laser pulse, II—fluorescence. a) SF_6, pulsed laser, b) BCl_3, LG-22 laser.

To obtain the required intensity, the laser radiation was focused with long-NaCl lenses. The cell with the investigated gases had two windows, one of silicon for the entry of the laser radiation, and one of lithium fluoride to register the fluorescence.

The laser pulse was registered with a photoresistor (GeAu, 77 °K) and the fluorescence ($\lambda = 0.4–1.1$ μ) was registered with a photomultiplier. Both signals were recorded with a two-beam oscilloscope triggered by the laser-pulse signal.

Typical fluorescence oscillograms are shown in Fig. 1. The fluorescence of SF_6 after irradiation with a 5-μsec pulse appears at a delay that depends on the gas pressure. The delay is 5 μsec at 20 Torr and 40 μsec at 2 Torr. A double emission pulse is observed at SF_6 pressure less than 12 Torr; at higher pressures, only the first pulse is preserved. The observed delay times are shorter than the V-T relaxation time, so that the fluorescence cannot be attributed to thermal dissociation.

The character of the visible emission of SF_6 and BCl_3 following irradiation by pulses of duration $\tau = 10^{-2}$

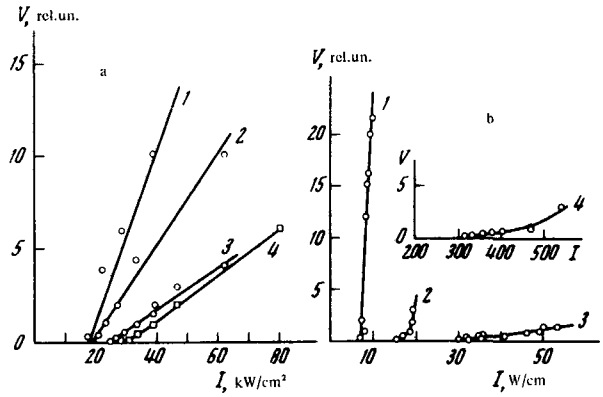

FIG. 2. Dependence of the intensity of the visible fluorescence on the intensity of the laser radiation: a) $\tau_p = 5$ μsec: 1—SF_6, $P = 20$ Torr, 2—SF_6, $P = 10$ Torr, 3—SF_6, $P = 4$ Torr, 4—SF_6, $P = 2$ Torr; b) $\tau_p = 50$ msec: 1—BCl_3, $P = 380$ Torr; 2—BCl_3, $P = 100$ Torr, 3—BCl_3, $P = 60$ Torr, 4—SF_6, $P = 380$ Torr.

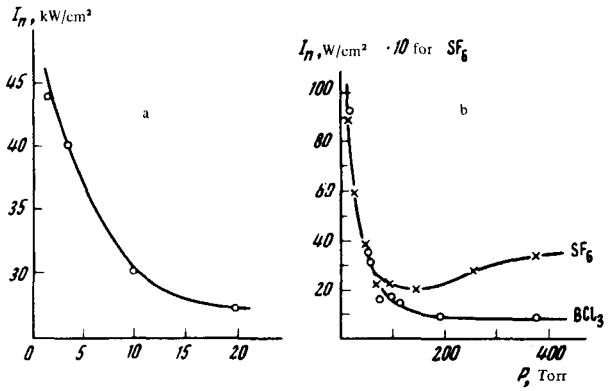

FIG. 3. Dependence of the visible-fluorescence thresholds on the absorbing-gas pressure: a—$\tau_p = 5$ μsec, b—$\tau_p = 50$ μsec.

– 1 sec depends on the gas pressure. At $P > 100$ Torr, two emission pulses are observed, the first with a delay 10–20 msec and lasting about 50 msec, and the second at 0.1 sec following the start of the irradiation and terminating in synchronism with the laser radiation. There is no double structure of the emission pulse at $P < 100$ Torr.

A study of the dependence of the SF_6 emission intensity on the laser intensity at short pulses ($\tau_p = 5$ μsec) has shown that the emission has a threshold (Fig. 2a). The threshold irradiation density decreases from 2.8×10^4 W/cm² at $P_{SF_6} = 2$ Torr to 1.7×10^4 W/cm² at $P_{SF_6} = 20$ Torr (Fig. 3a).

Similar plots were obtained for SF_6 and BCl_3 at an irradiation time 50 msec (Fig. 2b). The experiments have shown that the threshold character of the visible fluorescence is preserved under these conditions, and is more clearly pronounced for BCl_3 than for SF_6. The dependence of the fluoresence thresholds on the gas pressure at $\tau_p = 50$ msec is shown in Fig. 3. Attention is called to the rapid growth of the threshold irradiation intensity at $P < 100$ Torr, in the region where the threshold character of the emission becomes weaker (Fig. 2b). The reason why the threshold intensities increase with decreasing pressure under various irradiation regimes may be that the excitation of the higher vibrational levels of the molecules becomes more difficult if this excitation is of the collision type. It should be noted, however, that the threshold character of the molecule fluorescence, observed in the present study, does not follow from the results of theoretical papers devoted to resonant excitation of molecules by IR laser radiation.[10–13] The calculations in these papers are based on a single-mode model of the molecule. The interaction of the vibrational modes can lead[14] to a number of qualitative features in the mechanism of the resonant excitation of the higher vibrational levels. One of these features is the possibility that the molecule can store much more vibrational energy than in the case of a single mode. It appears that the interpretation of the observed effect should be sought along these lines.

[1)]These results were reported at the 8th Conference on Quantum Electronics in San Francisco (June 1974).

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